

AD629891

CARBORANE - SILOXANE ELASTOMERS

Report Period: 19 November 1965 through 18 February 1966

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REACTION MOTORS DIVISION
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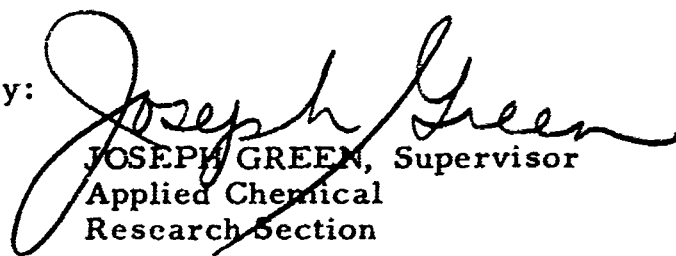
CARBORANE-SILOXANE ELASTOMERS

RMD Report 5065-Q4


Contract No. DA-11-070-AMC-852(W)

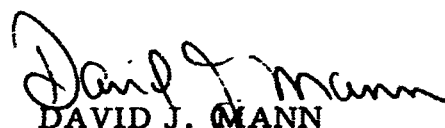
Report Period: 19 November 1965 through 18 February 1966

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FOREWORD

This report was prepared by Thiokol Chemical Corporation, Reaction Motors Division, under U. S. Army Contract No. DA-11-070-AMC-852(W). It covers work done in the fourth quarter of the program during the period 19 November 1965 through 18 February 1966. Mr. Z. T. Ossefort of Rock Island Arsenal is the Project Engineer. Contributors at Thiokol are: Mr. Nathan Mayes (Principal Scientist) and Mr. Alan Jackson.

ABSTRACT

The preparation of dicarboranyl alkanes by carboranylation of diacetylenic compounds and by alkylation of metallo carborane compounds was investigated. o-Carborane derivatives of such compounds were prepared by carboranylation of acetylenic compounds. Alkylation reactions yielded o-carborane exocycles and m-carborane low polymers.

A monomer, bis(1-chlorodimethylsilyl-o-carboran-2-yl) propane was prepared and its thermal isomerization to the m-carborane derivative was attempted.

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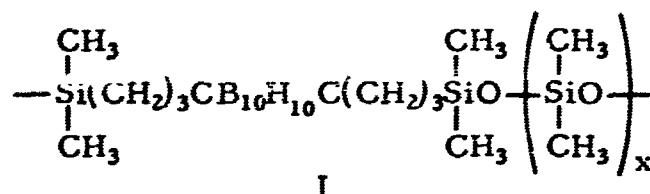
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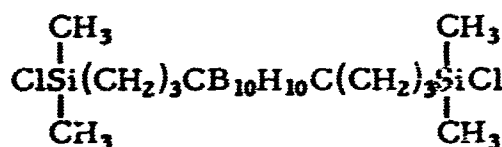
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I. INTRODUCTION

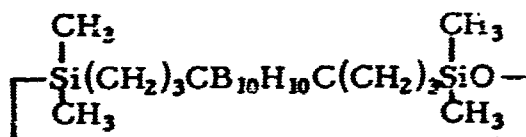
The objective of this program is the synthesis of thermally stable carborane siloxane elastomers. The initial approach toward this objective was the preparation of polymer structure* I where $x = 0, 1,$ and 2 .



During the first two quarters of the program, this approach led to the preparation of several precursors and monomers including



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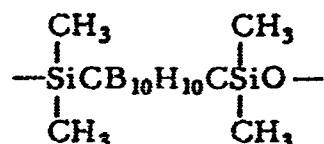


both of which were polymerized to polymers of the desired structures. The polymers were obtained as gums of molecular weights 5000-8500 and higher. The higher polymers did not dissolve and molecular weights are not known, but these materials were tough elastomeric gums of apparently high molecular weight and demonstrated the flexibility of the polymer chain.

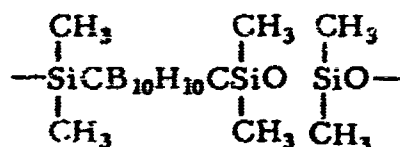
Evaluation of polymer structure I ($x = 0$) for thermal and thermal-oxidative stability indicated stability in inert atmosphere to 370°C (700°F) but decomposition in air at 240°C (465°F). These results indicated that carborane acted to retard the thermal rearrangements that polysiloxane chains ordinarily undergo, but it did not appreciably inhibit oxidative attack on the silyl methyl groups. With this knowledge, it became necessary to reexamine the approach that had been taken and to consider altering the course of the program.

* $-\text{CB}_{10}\text{H}_{10}-$ denotes 1,7-dicarboclovododecaborane commonly called m-carborane

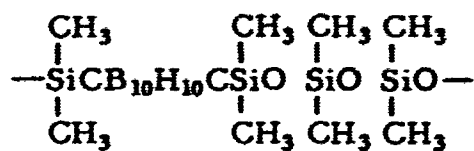
The reason for the lack of thermal-oxidative stability in the polymer under discussion became apparent upon examination of some recently published work concerning carborane siloxane polymers of somewhat different structure (Ref 1). These polymers, with structures II, III, IV, and V, contained carborane adjacent to silicon.



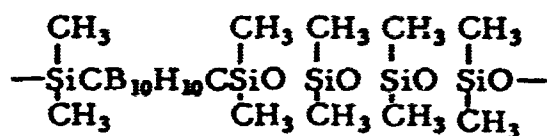
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III



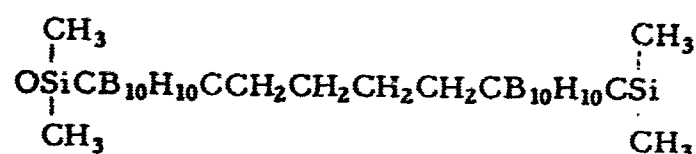
IV



V

Polymer of structure II, with carborane adjacent to every silicon, exhibited stability to 500°C in an inert atmosphere and to 450°C in air. The polymers of structures III, IV, and V exhibited progressively lower thermal oxidative stabilities. The data indicated that carborane stabilizes adjacent silyl methyl groups and protects them from oxidative attack. Silyl methyl groups farther removed from carborane, as in polymers III, IV, and V, were not protected, and lower thermal-oxidative stabilities were observed for these polymers. Thus, it was apparent that polymers of structure I were not stable to thermal-oxidative attack because in these structures the carborane group is too far from the silyl methyl groups to protect them.

It is evident then that to obtain carborane siloxane polymers of high thermal-oxidative stability, the carborane must be positioned adjacent to silicon as in structure II. Structure II, however, is a high melting resin (mp 200°C) and to obtain elasticity, it is necessary to incorporate flexible linking groups into the polymer chain. The linking groups may not be dimethylsiloxanes as in III, IV, and V because the methyl groups are not stabilized by carborane and are susceptible to oxidation. The linking groups then must also be adjacent to carborane, and in order to be within the known protective sphere of the carborane, the linking groups should contain no carbon atom that is more than one atom removed from carborane. Structure VI meets all of these requirements.



VI

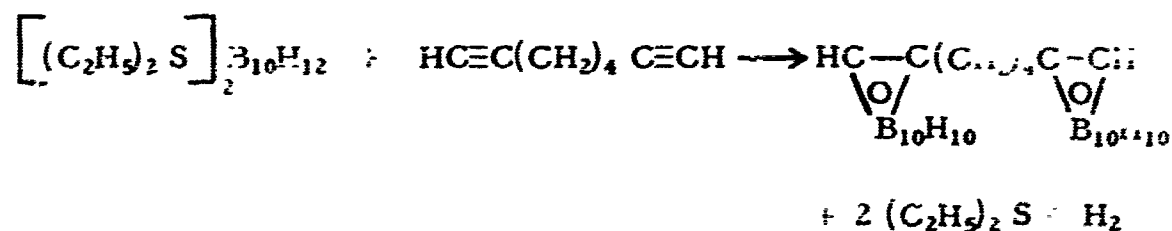
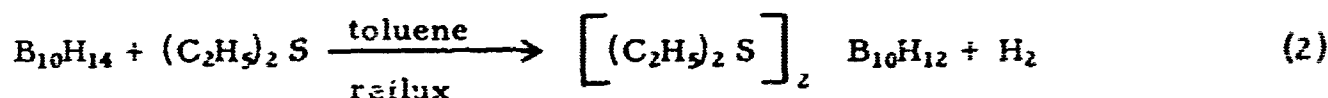
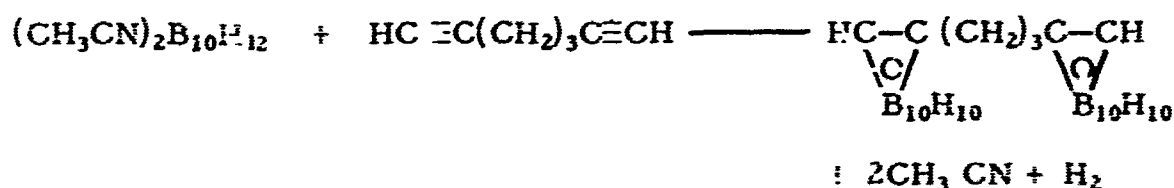
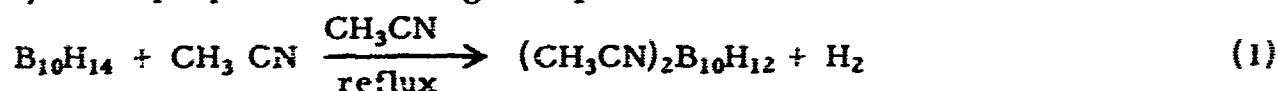
On the basis of the considerations discussed above, the course of the program was changed during the third quarter to allow preparation of structure VI and related structures. As a result, much of the third quarter and all of the fourth quarter has been devoted to the preparation of new carborane precursor materials and monomers.

II. TECHNICAL PROGRESS

A. PRECURSOR SYNTHESIS

The precursors necessary for the synthesis of monomers for the desired polymer structures are the following dicarboranylalkanes: 1,3-di-o-carboranylpropane, 1,3-di-m-carboranylpropane, 1,4-di-o-carboranylbutane, 1,4-di-m-carboranylbutane, 1,5-di-o-carboranypentane, and 1,5-di-m-carboranypentane. It was anticipated that the o-carborane derivatives would be synthesized most readily by direct carboranylation of the appropriate diacetylenic compound and that the m-carborane derivatives would have to be synthesized by alkylation of m-carborane.

The initial attempts to carboranylate diacetylenic compounds did yield some of the desired products; however, the yields were low (ca. 10%). The compounds prepared were 1,3-di-o-carboranylpropane and 1,4-di-o-carboranylbutane. They were prepared according to Equations 1 and 2.



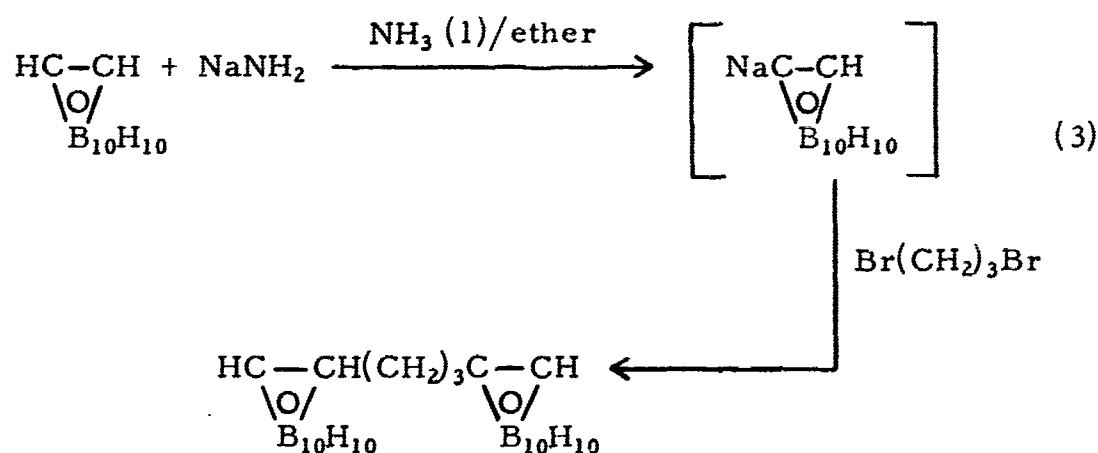
The low yields obtained prompted further investigation of the carboranylation reaction as well as alternate means of preparation.

In attempts to improve the yields, we found that altering reaction conditions such as reactant ratio, reaction time, solvent, and temperature did not substantially increase the yield. Difficulty in the carboranylation of diacetylenic compounds has been reported by Hawthorne (Ref 2), who determined that isolation of the monocarboranylated intermediate followed by further carboranylation to the desired product resulted in significantly higher yields. This approach was tried here for the preparation of 1,4-di-o-carboranylbutane. We found, however, that even the monocarboranylated product was formed in low yield and that the reaction was accompanied by gas evolution of the same order of magnitude as the yield. This showed that the low yields are not due to sluggish reaction of the second acetylenic group but are due to an as-yet undetermined difficulty of the primary carboranylation reaction.

In the course of this work, a new compound, the monocarboranylated product, 6-o-carboranylhexas-1-yne, was isolated. It was distilled as a colorless liquid (n_D^{20} 1.5401) at 114°/0.17 mm. It was identified by its infrared spectrum (Figure 1) and elemental analysis.

Analysis Calcd. for $C_8H_{20}B_{10}$: C, 42.81; H, 8.98; B, 48.21.
Found : C, 44.18; H, 9.27; B, 47.45.

The alternate procedure investigated for the preparation of dicarboranylalkanes was based on Zakharkin's reported alkylation of mono- and dimetallo carborane derivatives (Ref 3). We attempted to use this type of alkylation to prepare a di-o-carboranylalkane according to Equation 3.



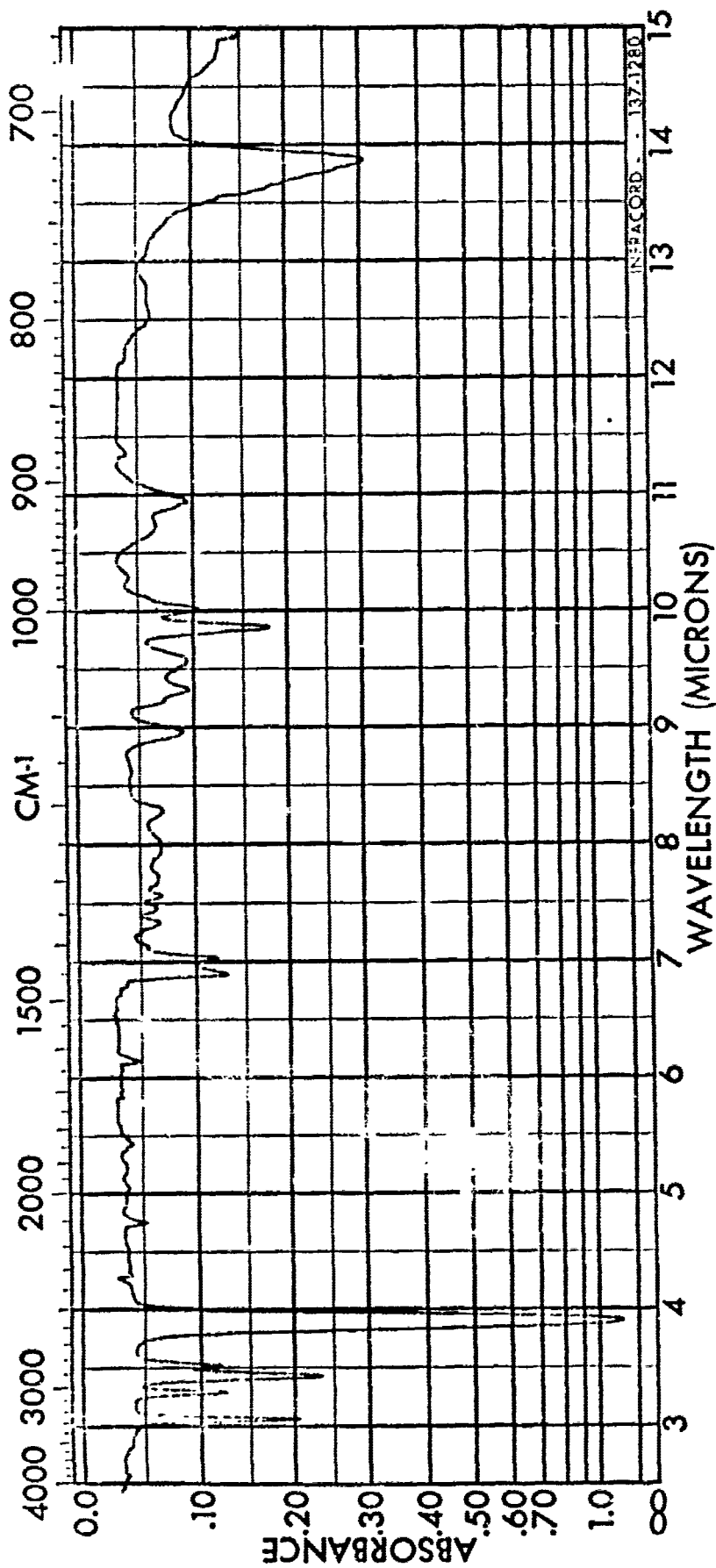
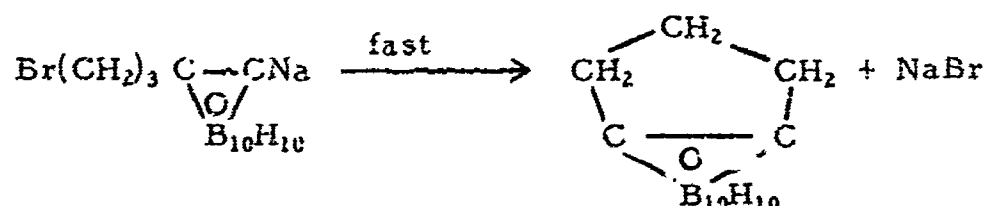
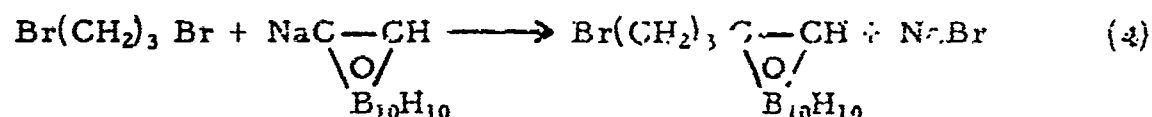


Figure 1. Infrared Spectrum of 6-o-Carboranylhax-1-yne

According to the literature, the intermediate monometallo carborane would form in at least 66% yield under the conditions used, and we expected that this would react as indicated in Equation 3. The product isolated from the reaction proved to be the cyclic 1,2- α -carboranycyclopentane (Ref 4). It forms, apparently, because a transmetalation equilibrium exists between metalated carborane and carborane having a free hydrogen. The equilibrium, as illustrated in Equation 4, is driven to the right in this case because a low energy path to cyclic formation exists.



The preparation of di- m -carboranylalkanes through alkylation of sodio- m -carborane was investigated. The reactions attempted were 1-sodio- m -carborane with 1,3-dibromopropane and with 1,4-dibromobutane. The m -carborane derivatives would not be expected to cyclize as did the α -carborane compounds. The reactions did not yield the desired dicarboranylalkanes, instead products that appear to be low polymers were obtained. One such product that was isolated and analyzed by infrared spectroscopy and elemental analysis is apparently either $\text{HCB}_{10}\text{H}_{10}\text{C}(\text{CH}_2)_3$, $\text{CB}_{10}\text{H}_{10}\text{C}(\text{CH}_2)_3\text{CB}_{10}\text{H}_{10}\text{CH}$ or $\text{HCB}_{10}\text{H}_{10}\text{C}(\text{CH}_2)_3[\text{CB}_{10}\text{H}_{10}\text{C}(\text{CH}_2)_3]_2\text{CB}_{10}\text{H}_{10}\text{CH}$. No solvent for this material could be found, hence, molecular weights could not be determined.

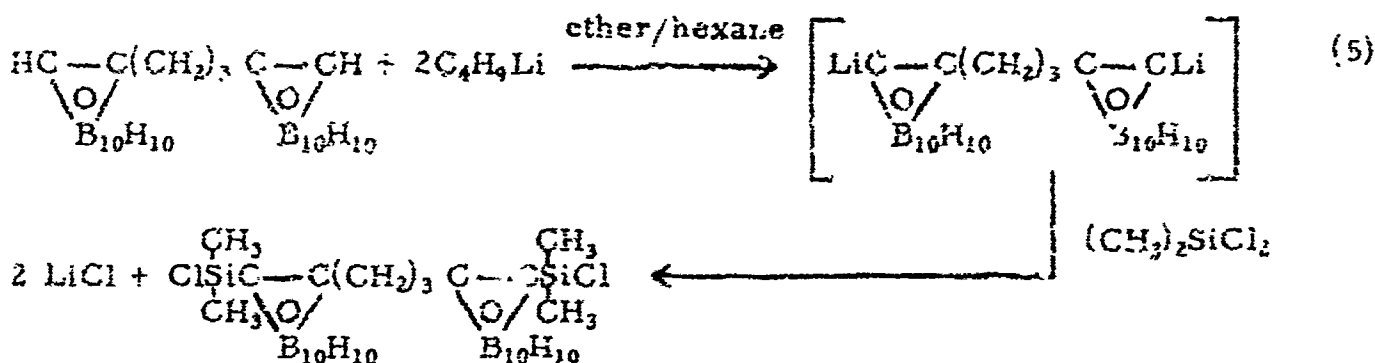
Analysis Calcd. for $\text{C}_7\text{H}_{28}\text{B}_{20}$: C, 25.5; H, 8.62; B, 65.8.
 $\text{C}_{12}\text{H}_{44}\text{B}_{30}$: C, 28.1; H, 8.65; B, 63.2.
 $\text{C}_{17}\text{H}_{60}\text{B}_{40}$: C, 29.3; H, 8.69; B, 62.0.

Found: C, 27.9; H, 8.58; B, 61.5.

B. MONOMER SYNTHESIS

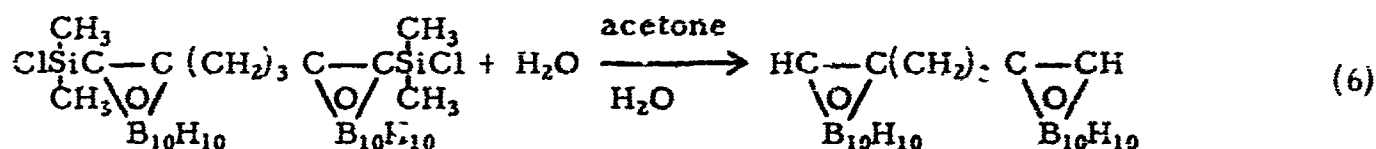
The monomers to be synthesized are the bis(chlorodimethylsilyl) derivatives of the dicarboranylalkanes named above. The first such monomer synthesized

was bis(1-chlorodimethylsilyl-o-carboran-2-yl)propane. This was prepared by treating the dilithio derivative of 1,3-di-o-carboranylpropane with a large excess of dichlorodimethylsilane (Equation 5).



The product, recrystallized once from heptane, was obtained in 60% yield as a solid of m. p. 200-205°C. It was identified by its infrared spectrum (Figure 2) and neutralization equivalent. Neutralization equivalent calculated: 156.8; found 157.9.

The compound hydrolyzed when treated with acetone and water, resulting in cleavage of the silicon-carborane bond and formation of the original di-o-carboranylalkane (Equation 6).



Bis(1-chlorodimethylsilyl-o-carboran-2-yl)propane was heated in an evacuated sealed Pyrex tube at 350°C for 18 hours in an attempt to isomerize it to the m-carborane isomer. The precedent for such a reaction is the quantitative isomerization of 1,2-bis(chlorodimethylsilyl)-o-carborane to the meta isomer (Ref 1) and similar isomerizations of variously substituted disilyl-o-carboranes (Ref 5). In the latter work, it was found that increasing substitution of large groups (phenyls) on silicon increased the strain on the C-C bond of o-carborane and lowered the temperature required for isomerization. Thiokol-RMD's efforts to isomerize bis(1-chlorodimethylsilyl-o-carboran-2-yl)propane have not been fully evaluated as of this writing; however, the infrared spectrum of the crude pyrolysis product (Figure 3) shows no substantial quantity of impurity, indicating no general decomposition. A new absorption present at 8.6 microns could be indicative of m-carborane. A quantity of unreacted starting material was recovered from the crude pyrolysis product leaving a material for which the infrared spectrum is identical to Figure 3 except that the absorption at 8.6 microns is somewhat stronger.

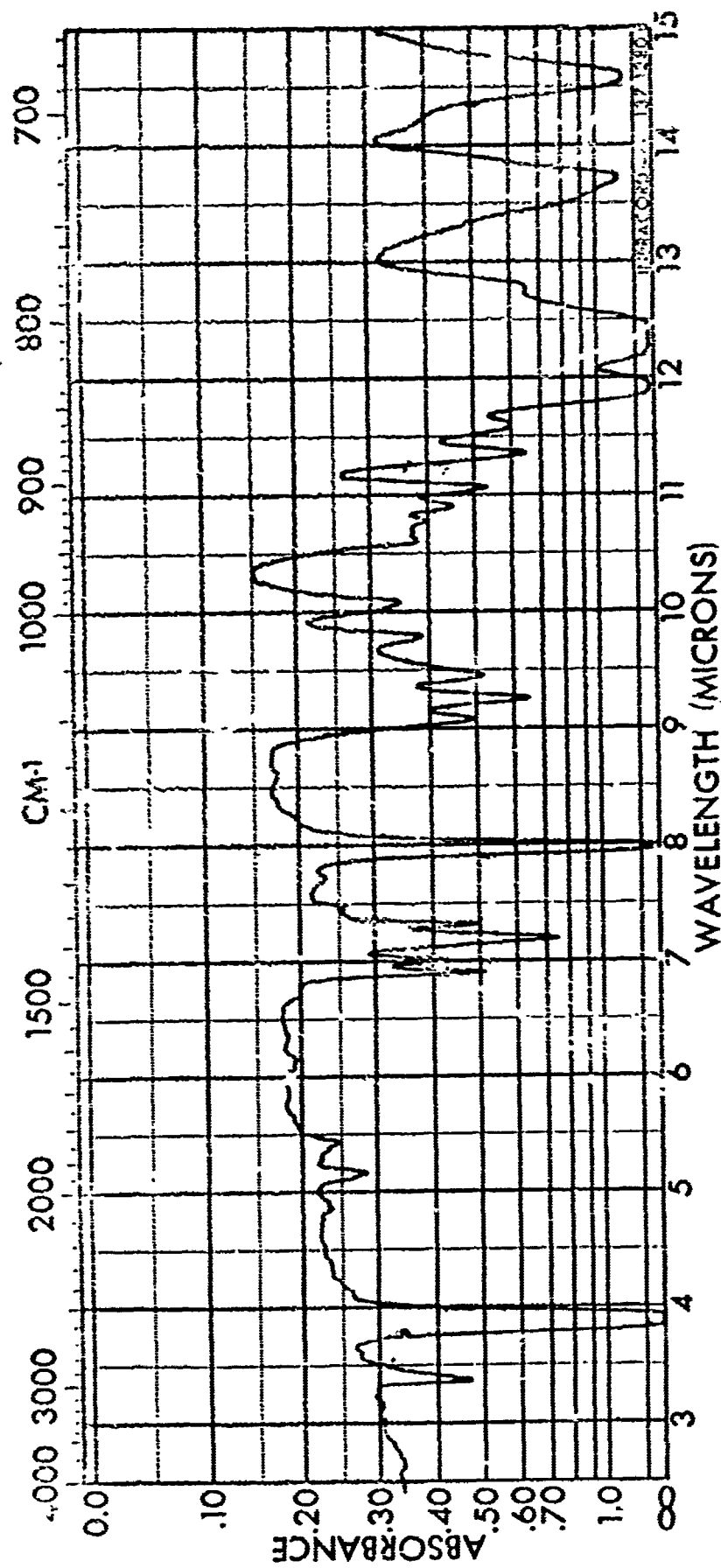


Figure 2. Infrared Spectrum of Bis(1-chlorodimethylsilyl-o-carboran-2-yl) propane

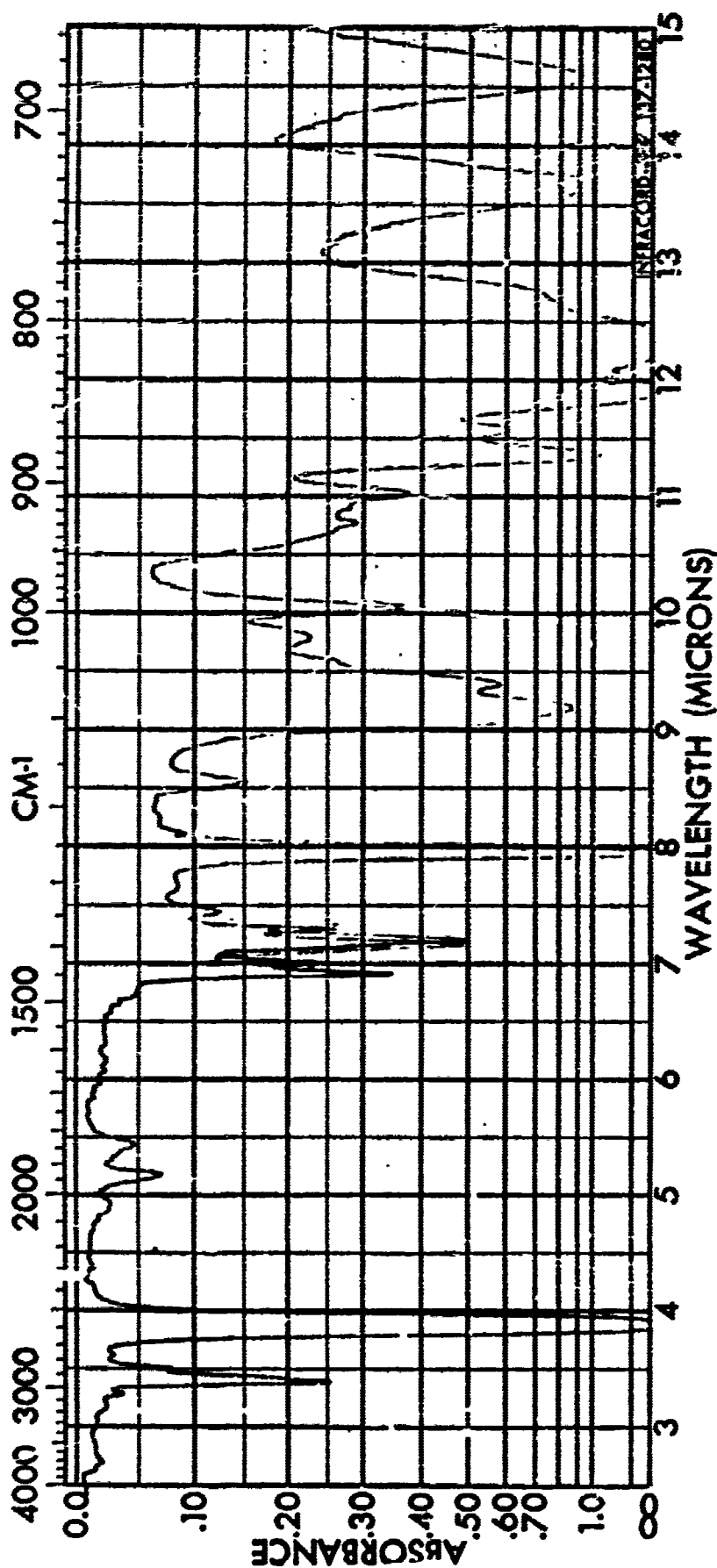


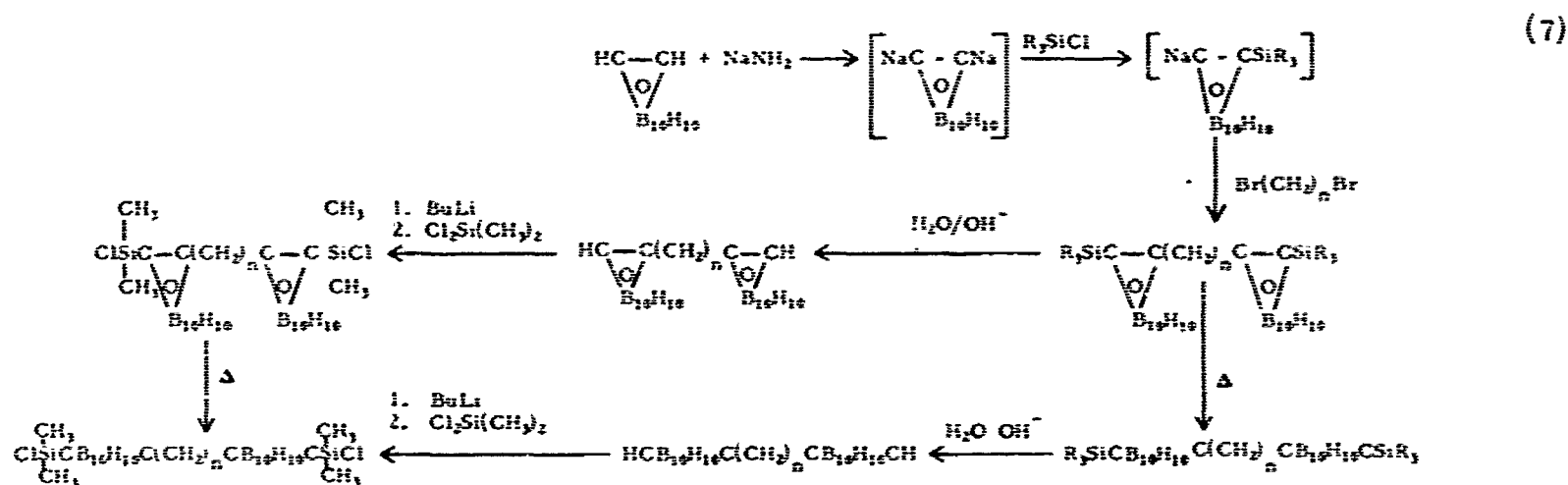
Figure 3. Infrared Spectrum of Bis(1-chlorodimethylsilyl-o-carboran-2-yl)propane After Pyrolysis at 350°C

III. DISCUSSION

This work has demonstrated that di-o-carboranylalkanes may be prepared by carboranylation of diacetylenic compounds; however, the low yields of these reactions are still unexplained. The complete investigation of the reaction that would be necessary to determine the optimum conditions to achieve high yields is beyond the scope of the present program. Since our primary objective is the preparation of polymer for evaluation, the work has been advanced toward this end with the preparation of monomers from the available precursor material.

Di-m-carboranylalkanes, the precursors for m-carborane silane monomers, cannot be prepared directly by carboranylation of acetylenic compounds. m-Carborane and its derivatives may be obtained only by thermal isomerization of o-carborane or o-carborane derivatives. In our efforts to prepare di-m-carboranylalkanes by alkylation of m-carborane, we obtained none of the desired products. This failure was due to the difficulty in limiting the alkylation to just one of the reactive sites of m-carborane. To accomplish this, it would be necessary to block one of the reactive sites, conduct the alkylation, and then regenerate the reactive site to permit substitution of a chlorodimethylsilyl group. There are no means that are readily apparent for doing this with m-carborane, but it is practical for o-carborane. If o-carborane compounds are prepared this way, their subsequent conversion to the meta derivatives by thermal rearrangement should be practical. The blocking group for o-carborane would be a trialkyl or triarylsilyl group of sufficient bulk that substitution of a second such group would be sterically hindered. The steric hindrance and the strain produced by two bulky groups on carborane have been demonstrated by the lower temperatures required to thermally isomerize such disubstituted carboranes (Ref 1, 5). Although substitution of a second bulky group would be hindered, alkylation would be permitted. The silyl blocking groups could be removed by base-catalyzed hydrolysis prior to the substitution of chlorodimethylsilyl

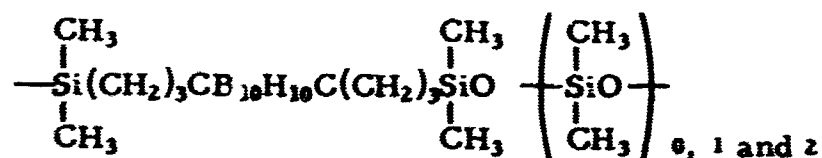
groups. This scheme (Equation 7) lends itself to the preparation of both o-carboranyl and m-carboranylsilane monomers.



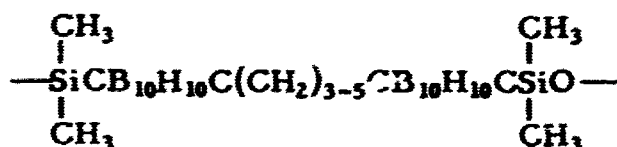
The monomer that has already been prepared in this work, bis(1-chloro-dimethylsilylcarboran-2-yl)propane, proved to be hydrolytically unstable, and it is therefore not polymerizable by the usual hydrolysis/condensation type reaction. It still may be polymerized, however, utilizing a silyl halide/silyl-alkoxide condensation reaction. This will necessitate the preparation of an alkoxide derivative. The hydrolytic cleavage of the carborane-silicon bond, even though it occurred without catalyst, was not entirely unexpected since acid and base catalyzed cleavage of o-carborane-silicon bonds has been observed before (Ref 6). We have seen that although a chlorosilane or a hydroxysilane carborane monomer may cleave in this manner, the siloxane polymer can be quite stable to hydrolysis (Ref 7).

IV. SUMMARY

The objective of this program is the preparation of a thermally stable carborane siloxane elastomer. The original approach taken to achieve the objective was the preparation of polymers of structure

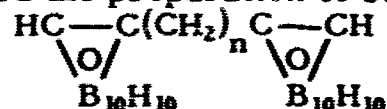


However, polymers of such structure were found to be susceptible to thermal oxidation. As a result, the approach was changed, with the new objective being the preparation of polymers of structure



These polymers may be stable to thermal oxidation through stabilization of silyl methyl groups and alkyl linking groups by the inductive or energy sink effect of nearby carborane groups.

Toward the preparation of such polymers, o-carborane precursors of structure



where $n = 3$ and 4 , were prepared by carboranylation of diacetylenic compounds. Attempts to prepare such compounds — as well as m-carborane isomers of such compounds — by alkylation reactions failed.

The monomer bis(1-chlorodimethylsilylcarboran-2-yl)propane was prepared. It was found to hydrolyze with cleavage at the carborane-silicon bond and, therefore, it may not be polymerized by the hydrolysis/condensation process. It will have to be polymerized by the silylhalide/silylalkoxide condensation reaction. This monomer, by analogy to other disilyl carborane compounds, may be expected to thermally rearrange to the m-carborane derivative. Studies of this rearrangement were started and initial results show promise for the reaction.

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7. Thiokol Chemical Corporation, Reaction Motors Division, Unpublished data

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| 13. ABSTRACT <p>The preparation of dicarboranyl alkanes by carboranylation of diacetylenic compounds and by alkylation of metallo carborane compounds was investigated. <u>o</u>-Carborane derivatives of such compounds were prepared by carboranylation of acetylenic compounds. Alkylation reactions yielded <u>o</u>-carborane exocycles and <u>m</u>-carborane low polymers.</p> <p>A monomer, bis(1-chlorodimethylsilyl-<u>o</u>-carboran-2-yl) propane, was prepared and its thermal isomerization to the <u>m</u>-carborane derivative was attempted.</p> | | |

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